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Complete Specification  
entitled (54)

PROCESS FOR THE CONVERSION OF METAL SULPHIDE  
ORES TO SULPHATES AND ELEMENTAL SULPHUR WITH  
INSOLUBILISATION OF THE IRON CONTENT OF THE ORE

(Na<sub>2</sub>Co<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)

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Nil

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Related Art (56) Nil

The following statement is a full description of this invention, including the best method of performing it known  
to us :

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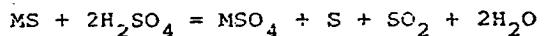
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## BACKGROUND OF INVENTION

A number of pyrometallurgical and hydrometallurgical processes exist for the extraction of nickel, cobalt, copper and zinc from sulphide ores, in which they are generally associated with iron sulphides. Each of the existing processes has certain disadvantages - the smelting processes produce sulphur dioxide, only part of which can be recovered, the remainder polluting the atmosphere. Ammonia-leaching produces large quantities of by-product ammonium sulphate for which there is generally insufficient local market.

## SUMMARY OF INVENTION

The process which is the subject of this invention utilises the reaction of the metal sulphide with concentrated sulphuric acid to produce the metal sulphate and elemental sulphur, two desirable products, and avoids pollution of the atmosphere. The metal sulphate can be treated by known hydrometallurgical means to yield the metal, and the elemental sulphur can be sold. The reactions believed to occur between 150 and 300°C include:



This reaction is found to be endothermic for all five metals, nickel, cobalt, copper, zinc and iron, so that heat must be supplied to sustain the reaction.

The application of this reaction to the treatment of nickel sulphide was first established in our laboratory by heating 1 part by weight of a nickel sulphide concentrate (assay 12.2% Ni, 12.4% Fe, 18.7% S), with 2.3 parts by weight of concentrated sulphuric acid. Sulphur and

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sulphur dioxide were volatilised and the former condensed, and nickel and iron sulphates were found in the residue.

Of the quantities present in the original concentrate 91% of the nickel and 93% of the iron were found as soluble sulphates in the residue, and 93.5% of the sulphur was extracted by carbon disulphide from the sublimate.

A further test was made with another nickel concentrate from a different source, consisting of pentlandite and pyrrhotite. Quantitative results were not sought but the reaction was observed to proceed in the same manner as for the first concentrate.

The application of the reaction to zinc sulphide ores was established by means of a quantitative test similar to that described for nickel. One part by weight of a mixed lead-zinc bulk concentrate (assay 8.3% Pb, 26.0% Zn, 14.1% Fe, 29.2% S, consisting of galena, sphalerite, pyrite and gangue) was heated with 2.3 parts by weight of concentrated sulphuric acid. Metal recoveries as sulphates in the residue were Pb 95%, Zn 95% and Fe 96.5% and sulphur recovery by extraction of the sublimate with carbon disulphide amounted to 96% of that originally present in the concentrate.

Treatment of the metal sulphates to produce a leach solution low in soluble iron forms a further step of this invention.

The preferred method of carrying out the above reaction is in a fluid bed reactor using a granular carrier material such as coarse sand as a bed medium. A slurry of

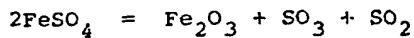
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sulphide concentrate and concentrated sulphuric acid is injected into the bed whereupon the sulphides react with the  $H_2SO_4$  and partially coat the particles of the bed material. The off-gases consisting of sulphur vapour, sulphur dioxide and steam containing fine solids pass to a hot cyclone for removal of entrained solids, thence to sulphur condensation and conversion of  $SO_2$  to sulphuric acid.

According to the first part of this invention the roasted bed material is leached in water whereas the second part involves the application of a further roasting stage to the bed material. The roasted bed material contains silica sand, metal sulphates and insoluble gangue. Any iron in the ore will have been converted to iron sulphate. If this product were directly leached, a leach solution high in iron would be produced. This is undesirable for later processing steps, in that nickel has to be separated from iron, and sulphuric acid has to be produced from hydrated iron sulphate. However, it is possible to decompose the iron sulphate to insoluble iron oxide and a gas mixture of  $SO_2$  and  $SO_3$ , by a further roasting step at a temperature above  $480^{\circ}C$  and probably selected within the range  $600-750^{\circ}C$ . The temperature of the second stage roast will depend upon the specific ore being heated. The desired second stage roasting temperatures for recovery of the relevant sulphates are copper 600 to  $650^{\circ}C$ . Nickel 700 to  $750^{\circ}C$ , Cobalt 700 to  $750^{\circ}C$  Zinc 700 to  $750^{\circ}C$  and Lead 650 to  $700^{\circ}C$ . In these respective temperature ranges the sulphates of Cu, Ni, Co, Zn and Pb are stable and will not appreciably decompose.

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The relevant reaction is:



The preferred method of carrying out the second roast is again in a fluid bed reactor. The sulphur oxides given off in this roasting stage can be recovered and converted to  $\text{H}_2\text{SO}_4$  for recycling to the first stage.

After the second stage roast the bed material can be leached in water and a solution low in iron and containing the metal values separated for further treatment. The sand can be separated from the insoluble iron oxide by sizing or magnetic separation or a combination of the two, and recycled to the sulphation roasting stage (Stage 1).

#### DESCRIPTION OF THE FLOWSHEET

The overall process consists of two roasting stages, sulphation and iron sulphate decomposition, either in one two-stage fluid bed unit or in separate reactors as shown in the diagram. The slurry of sulphide concentrate in sulphuric acid is admitted, together with recycled sand, to the first stage reactor 1 which is the sulphation stage and is maintained at  $150\text{--}300^\circ\text{C}$ . The reactor is heated and the bed fluidised by the off-gases from the second stage reactor 2 which is the subsequent iron sulphate decomposition stage. The off-gases from the sulphation roast stage 1 are scrubbed with water in the unit 3 recover elemental sulphur and then pass to a contact acid-plant 4. All the acid produced is recycled back to the sulphation stage 1.

The roasted products from the sulphation stage 1 pass to the second stage reactor 2 which is maintained

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at 600-750°C by direct oil firing. The iron sulphate decomposes and the off-gases provide the fluidising and heating gas for the first sulphation stage reactor 1. The roasted product is leached in water in the leaching vessel 5, and the leach solution separated, and the residue treated for the removal of Fe<sub>2</sub>O<sub>3</sub> in the separator 6. The sand is then recycled to the first reactor 1.

The products by the total process are, metal sulphate solutions (Cu, Ni, Co, Zn), elemental sulphur, and iron oxide. By using different leaching solutions lead and silver may also be extracted.

### EXAMPLE 1

One example of the invention may be cited in the treatment of a nickel sulphide concentrate containing 11.0% Ni. The concentrate was slurried with concentrated H<sub>2</sub>SO<sub>4</sub> and reacted at 250°C. The residue was split and one half leached in water and one half roasted at 700°C for one hour in a muffle furnace and then leached in water. Both leach solutions were assayed for Ni and Fe. The nickel extraction was high in both liquors (95-100%). The iron extraction was 88.7% in the first liquor and 15.5% in the second liquor.

The results show that a second stage higher temperature roast (~700°C) is effective in reducing the soluble iron content while not markedly affecting the soluble nickel content. The results also suggest a higher temperature second stage (~750°C for nickel concentrates) would further

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reduce the soluble iron content without a detrimental effect on nickel recovery.

## EXAMPLE 2

Another example may be cited in the treatment of a copper-arsenic concentrate containing 9.1% iron. The concentrate was slurried as in example 1 with concentrated sulphuric acid and reacted at 250°C. The residue was split and one half leached in water and one half roasted at 700°C, but in this case for only one half hour, in a furnace and then leached in water. Both leach solutions were assayed for Cu, and Fe. The copper extraction was high in both liquors, but the iron extraction was 72.2% in the first liquor and 0.01% in the second liquor.

The result again showed that a second stage higher temperature roast is effective in reducing the soluble iron content while not affecting the soluble copper content.

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The claims defining the invention are as follows:-

1. The process for the conversion of metal sulphide ores to sulphates and elemental sulphur wherein the concentrate together with sulphuric acid and recycled carrier material is passed to a fluid bed reactor, maintaining the reactor at a temperature of 150 to 300°C to effect sulphation, passing the off-gases from the sulphation stage to a recovery unit utilising water scrubbing to recover elemental sulphur, passing the residual sulphur dioxide to a contact acid plant, recycling the sulphuric acid from the contact acid plant back to the reactor, and passing the carrier material with adhering metal compounds to a leaching stage to separate the pregnant solution, and passing the carrier material back to the reactor.
2. A process of claim 1 for the conversion of metal sulphide ores to sulphates and elemental sulphur with insolubilisation of the iron content of the ore, comprising subjecting the carrier material with adhering metal compounds before leaching to roasting in a fluid bed reactor having a temperature exceeding 480°C, passing the off-gases consisting of sulphur dioxide and steam to a cyclone separator for removal of entrained solids.
3. The process of claim 2 wherein the temperature is between 600°C and 750°C to selectively decompose the iron sulphates.

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4. The process for the conversion of metal sulphide ores to sulphates and elemental sulphur with insolubilisation of the iron content of the ores, comprising subjecting a slurry of sulphide concentrates to a first temperature of between 150 and 300°C in a reactor in the presence of a carrier material and sulphuric acid, recovering elemental sulphur from the off-gases from this stage, converting the residual sulphur dioxide to sulphuric acid for recycling, passing the carrier material and metal compounds from the first reactor to a second reactor, maintaining a temperature in the second reactor of between 600°C and 750°C, passing the carrier material and metal compounds to a leaching vessel to recover the carrier material, recycling the carrier material to the first reactor, and recovering the metals.

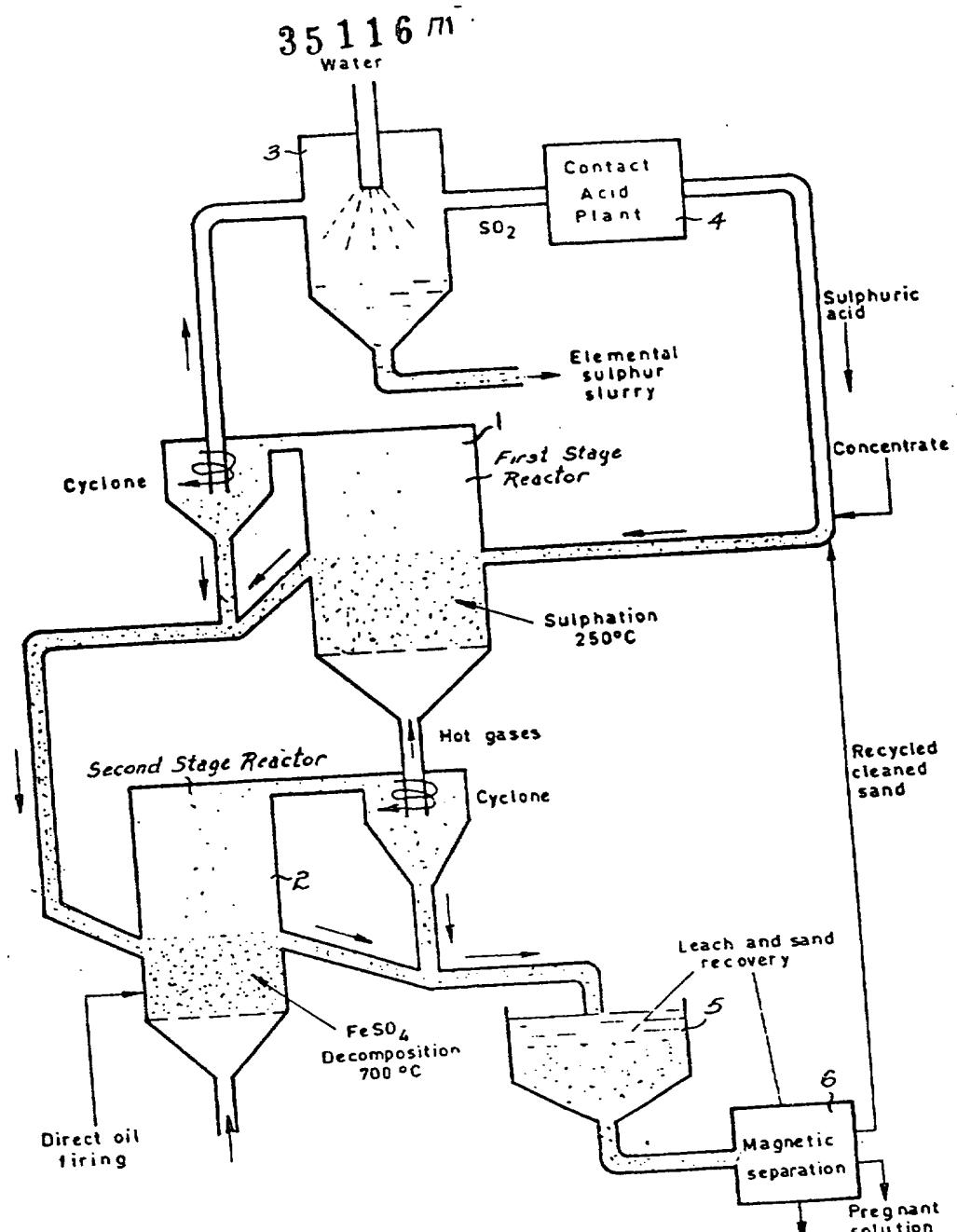
5. The process of claim 4 wherein the carrier material is coarse sand.

6. The process of claim 3 wherein the second stage reactor is fired and the hot gases passed to the first stage reactor, each reactor having a cyclone associated with its gaseous output to recover entrained solids.

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FLOWSHEET EMPLOYING TWO FLUID BED  
REACTOR STAGES